Journal of Organometallic Chemistry, 412 (1991) 451–456
Elsevier Sequoia S.A., Lausanne
JOM 21866

Synthesis and NMR spectroscopy of five-coordinate platinum(II) hydride complexes

Andreas Handler, Paul Peringer *
Institut für Anorganische und Analytische Chemie der Universität Innsbruck, Innrain 52a, A-6020 Innsbruck (Austria)

and Ernst P. Müller
Institut für Organische und Pharmazeutische Chemie der Universität Innsbruck, Innrain 52a, A-6020 Innsbruck (Austria)

(Received February 25th, 1991)

Abstract

Treatment of $[Pt\{PhP(CH_2CH_2PPh_2)_2\}(PPh_3)](O_3SCF_3)_2$ with $NaBH_4$ gives the five-coordinate platinum hydride complex $[PtH\{PhP(CH_2CH_2PPh_2)_2\}(PPh_3)]^+$ or $[Pt\{PhP(CH_2CH_2PPh_2)_2\}(PPh_3)]$ depending on the reaction conditions. The zerovalent complex and the hydride are readily interconverted. The hydride complexes $[PtH\{PhP(CH_2CH_2PPh_2)_2\}L]^+$, L = PBu_3, PPh_2H, PCy_2H (Cy = cyclohexyl) and $Ph_2PCH_2PPh_2$ have also been prepared.

Introduction

Oxidative addition of protic compounds to various platinum(0) phosphine complexes is known to produce hydridoplatinum(II) complexes: thus the reaction of the two-coordinate species $[Pt(PPh^tBu_2)_2]$ with proton acids HX was shown to give $[PtHX(PPh^tBu_2)_2]$ [1]. For $X = MeO^-$, subsequent β-H elimination leads to $[PtH_2(PPh^tBu_2)_2]$. The three-coordinate complex $[Pt(P^iPr_3)_3]$ is protonated by ROH to give $[PtH(P^iPr_3)_3]^+$ [2]. The protonation of $[Pt_2(\mu\text{-}Ph_2PCH_2PPh_2)_3]$ with NH_4PF_6 gives $[Pt_2H(\mu\text{-}Ph_2PCH_2PPh_2)_2(Ph_2PCH_2PPh_2\text{-}P)]^+$ whereas $[Pt_2(\mu\text{-}Et_2PCH_2PEt_2)_3]$ and $[Pt_2(\mu\text{-}Me_2PCH_2PMe_2)_3(PPh_3)]$ give the dihydrides $[Pt_2H_2(\mu\text{-}R_2PCH_2PR_2)_3]^{2+}$ (R = Me or Et) [3]. The four-coordinate complex $[Pt(PEt_3)_4]$ was reported to react with ROH to yield $[PtH(PEt_3)_3]^+$ [4]. At very low temperatures (−130 °C) $[PtH(PEt_3)_4]^+$ is formed according to eq. 1 [5].

$$[PtH(PEt_3)_3]^+ + PEt_3 \rightleftharpoons [PtH(PEt_3)_4]^+ \qquad (1)$$

Very recently $[Pt\{P(CH_2OH)_3\}_4]$ was reported to react reversibly with ROH or H_2O according to eq. 2 [6].

$$[Pt\{P(CH_2OH)_3\}_4] + H^+ \rightleftharpoons [PtH\{P(CH_2OH)_3\}_4] \qquad (2)$$

0022-328X/91/$03.50

We report here the synthesis of the five-coordinate platinum hydride complex $[PtH\{PhP(CH_2CH_2PPh_2)_2\}(PPh_3)]^+$, which readily undergoes conversion into the corresponding zerovalent complex $[Pt\{PhP(CH_2CH_2PPh_2)_2\}(PPh_3)]$.

Experimental

The NMR spectra were recorded on Bruker WP-80 and AM-300 instruments. Elemental analyses were carried out by the Institut für physikalische Chemie der Universität Wien.

Preparation of compounds

All experiments were carried out in dried solvents under dinitrogen. $[Pt\{PhP(CH_2CH_2PPh_2)_2\}(PPh_2H)](O_3SCF_3)_2$ and $[Pt\{PhP(CH_2CH_2PPh)_2\}(PCy_2H)](O_3SCF_3)_2$ were prepared as described previously [7]. $[Pt\{PhP(CH_2CH_2PPh_2)_2\}(PPh_3)](O_3SCF_3)_2$, $[Pt\{PhP(CH_2CH_2PPh_2)_2\}(PBu_3)](O_3SCF_3)_2$ and $[Pt\{PhP(CH_2CH_2PPh_2)_2\}(Ph_2PCH_2PPh_2)](O_3SCF_3)_2$ were obtained analogously. All other reagents were from commercial sources.

Preparation of $[PtH\{PhP(CH_2CH_2PPh_2)_2\}(PPh_3)]BPh_4$

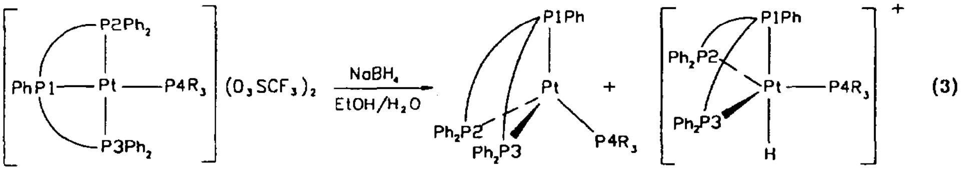
$NaBH_4$ (18.9 mg, 0.5 mmol) was added to a solution of $[Pt(PhP(CH_2CH_2PPh_2)_2\}(PPh_3)](O_3SCF_3)_2$ (129.0 mg, 0.1 mmol) in methanol (0.4 mL) and dichloromethane (0.4 mL) and the mixture stirred for 10 min. The volume of the solution was reduced *in vacuo* to ca. 0.3 mL. Addition of $NaBPh_4$ (34.2 mg, 0.1 mmol) in methanol (0.2 mL) gave a precipitate, which was filtered off, washed with water (2 × 0.5 mL) and methanol (2 × 0.3 mL), and dried *in vacuo*. M.p. 117–118°C. Found: C 65.6, H 4.9. $C_{76}H_{69}BP_4Pt \cdot CH_2Cl_2$ calc.: C 66.19; H 5.12%.

The same procedure was used for: $[PtH\{PhP(CH_2CH_2PPh_2)_2\}(PBu_3)]BPh_4$, m.p. 140–142°C. Found: C 66.8, H 6.4. $C_{70}H_{81}BP_4Pt$ calc.: C 67.14, H 6.52%. $[PtH\{PhP(CH_2CH_2PPh_2)_2\}(Ph_2PCH_2PPh_2)]BPh_4$, m.p. 161°C. Found: C 67.6, H 5.4. $C_{83}H_{76}BP_5Pt \cdot 0.5CH_2Cl_2$ calc.: C 67.91, H 5.26%. δ P1 = 60.2, δ P2,3 = 32.3, δ P4 = −4.4, δ P5 (uncoordinated ($Ph_2PCH_2PPh_2$) phosphorus) = −27.8, J(PtP1) = 1715, J(PtP2,3) = 2797, J(PtP4) = 2887, J(PtP5) = 84, J(P1P4) = 20, J(P2P4) = 141, J(P3P4) = 162, J(P4P5) = 119, J(P1H) (hydride) = 171, J(PtH) = 614, δ Pt = −5467 (243 K). $[PtH\{PhP(CH_2CH_2PPh_2)_2\}(PPh_2H)]BPh_4$, m.p. 172–174°C, Found: C 66.0, H 5.1. $C_{70}H_{65}BP_4Pt \cdot 0.5CH_2Cl_2$ calc.: C 66.23, H 5.20%. δ P1 = 65.0, δ P2,3 = 34.5, δ P4 = −23.6. J(PtP1) = 1668, J(PtP2,3) = 2905, J(PtP4) = 2632, J(P2,3P4) = 139, J(P1H) = 156, J(PtH) = 656, δ Pt = −5600 (213 K). $[PtH\{PhP(CH_2CH_2PPh_2)_2\}(PCy_2H)]O_3SCF_3 \cdot NaBH_4$ (18.9 mg, 0.5 mmol) was added to a solution of $[Pt\{PhP(CH_2CH_2PPh_2)_2\}(PCy_2H)](O_3SCF_3)_2$ (122.6 mg, 0.1 mmol) in methanol (0.4 mL) and dichloromethane (0.4 mL) and the mixture was stirred for 10 min, and the volume of solvent then reduced to ca. 0.3 mL. After addition of methanol (0.7 mL) the product was collected by filtration, washed with water (2 × 0.5 mL) and dried *in vacuo*. M.p. 174°C. Found: C 52.3, H 5.2. $C_{47}H_{57}O_3P_4PtS$ calc.: C 52.37, H 5.33%. δ P1 = 60.9, δ P2,3 = 34.6, δ P4 = −9.4, J(PtP1) = 1701, J(PtP2,3) = 2865, J(PtP4) = 2588, J(P1P2) = 6, J(P1P3) = 6, J(P1P4) = 16, J(P2P4) = 138, J(P3P4) = 130, J(P1H) = 164, J(PtH) = 600, δ Pt = −5683 (213 K).

Results and discussion

A standard procedure for the preparation of zerovalent platinum tetraphosphine complexes involves treatment of the corresponding Pt^{II} complex with $NaBH_4$ in aqueous ethanol [8,9]. The zerovalent platinum complexes are usually insoluble in this solvent and separate out.

During the synthesis of $[Pt\{PhP(CH_2CH_2PPh_2)_2\}(PPh_3)]$ by this method we noted that the ethanol–water filtrate contained a small amount of a compound that was subsequently identified as the hydridoplatinum(II) complex $[PtH\{PhP(CH_2CH_2PPh_2)_2\}(PPh_3)]^+$ (eq. 3).



1a **1b** **1c**

Complex **1c** is also progressively formed upon addition of methanol to a solution of **1b** in dichloromethane. For example, a solvent composition methanol/dichloromethane of 1/8 results in a ratio **1b**/**1c** of ca. 0.6/1 as estimated by the integration of the ^{31}P NMR signals. The patterns of both species are discernible in the ^{31}P NMR spectrum, and this shows that the proton transfer between **1b** and **1c** is slow on the NMR time scale. Addition of water to this methanol–dichloromethane mixture regenerates **1b**, presumably by extraction of methanol into the aqueous phase.

The hydride **1c** is formed quantitatively upon reduction of **1a** with $NaBH_4$ in methanol–dichloromethane. The reaction could in principle proceed either by direct hydride transfer from the boranate ion or via the zerovalent platinum complex **1b**, followed by the oxidative addition of the solvent methanol. When the reaction was carried out in methanol-d_4–dichloromethane as solvent, $[Pt^1H\{PhP(CH_2CH_2PPh_2)_2\}(PPh_3)]$ was formed, demonstrating that the first possibility was the correct one. The hydride complex **1c** generated by reduction of **1a** in methanol–dichloromethane is not converted into **1b** upon addition of water, but evaporation of the solvent *in vacuo* and redissolution in toluene gives **1b**.

Treatment of **1a** with $NaBH_4$ in dichloromethane–water gives the hydride **1c**, whilst in aqueous tetrahydrofuran the zerovalent complex **1b** is formed.

NMR spectroscopy

The complexes **1a**, **1b** and **1c** were characterized by ^1H, ^{31}P and ^{195}Pt NMR spectroscopy, the data are summarized in Table 1. The NMR spectra of **1a** closely resemble those of $[Pt\{PhP(CH_2CH_2PPh_2)_2\}(PR_2H)](O_3SCF_3)_2$, which were reported previously [7].

The ^{31}P NMR spectrum of **1b** is consistent with the structure indicated in eq. 1. The signal at 44.1 ppm is assigned to the central phosphorus atom P1 of the $PPh(CH_2CH_2PPh_2)_2$ ligand by comparison to $[Pt\{PhP(CH_2CH_2PPh_2)_2\}(PBu_3)]$ (*vide infra*). This phosphorus couples nearly equivalently to the terminal phosphorus atoms P2 and P3 and to triphenylphosphine (P4) to produce a quartet

Table 1

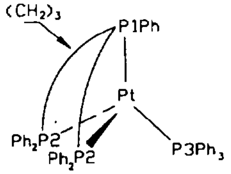
NMR parameters[a]

	1a	**1b**[b]	**1c**	**2a**	**2b**[b]	**2c**
δ P1 (*J*(PtP1))	94.8 (2130)	44.1 (3014)	59.9 (1770)	97.7 (1978)	45.8 (2987)	60.8 (1763)
δ P2,3 (*J*(PtP2,3))	44.0 (2365)	25.4 (3658)	33.6 (2844)	44.8 (2422)	27.1 (3608)	34.3 (2702)
δ P4 (*J*(PtP4))	13.3 (2584)	25.5 (4683)	7.3 (2746)	−1.9 (2345)	−6.6 (4524)	−18.2 (2798)
δ H			−9.9			−10.0
δ Pt		−5187[c]			−5259[c]	−5584[c]
J(P1P2)		75	6		74	6
J(P1P3)		75	6		74	6
J(P1P4)	294	75	19	281	67	18
J(P2P4)	14	75	137	17	67	156
J(P3P4)	14		143	17		141
J(P1H)			169			170
J(P2,3H)			3			3
J(P4H)			20			22
J(PtH)			617			633
T (K)	300	300	243	300	300	300

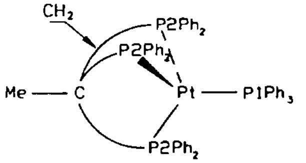
[a] Chemical shifts relative to 85% H_3PO_4, 1 *M* Na_2PtCl_6 or TMS, coupling constants in hertz, solvent CH_3OH/CH_2Cl_2 unless otherwise stated. [b] Solvent toluene. [c] 223 K ddt (d = doublet, t = triplet).

pattern. The phosphorus atoms 2,3 and 4 give rise to an AB_2 spin system, which was analyzed to yield δ P2 and δ P3 = 25.4 ppm and δ P4 = 25.5 ppm with a coupling constant of 75 Hz.

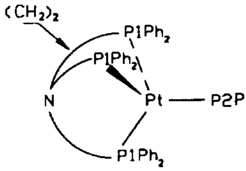
The Pt–P coupling constants of **1b** are very different, ranging from 4683 Hz for the PPh_3 ligand to 3014 Hz for the central phosphorus of the $PPh(CH_2CH_2PPh_2)_2$ ligand. A similar effect was observed for other zerovalent platinum complexes coordinated by one tridentate and one monodentate phosphine ligand:



JPtP1 = 3994
JPtP2 = 3664
JPtP3 = 3356
Ref. 8



JPtP1 = 5400
JPtP2 = 3096
Ref. 9



JPtP1 = 3657
JPtP2 = 4438
Ref. 10

It was interpreted in terms of the differing *s*-characters of the Pt–P bonds [9]; for example, since the tridentate ligand $CH_3C(CH_2PPh_2)_3$ forms P–Pt–P angles of 93–94°, these Pt–P bonds will have less *s*-character than Pt–P bonds in regular tetrahedral geometry. The Pt–PPh_3 bond will be hybridized to have more *s*-character, giving rise to a larger coupling constant. From this point of view it is of interest to compare the Pt–P coupling constants of **1b** with those of $[Pt\{PhP(CH_2CH_2CH_2PPh_2)_2\}(PPh_3)]$ which involves two six-membered chelate rings rather than the five-membered rings in **1b**.

A trigonal bipyramidal structure is postulated on the basis of NMR evidence for the hydride **1c**. As indicated in eq. 1, the central phosphorus of the $PPh(CH_2CH_2PPh_2)_2$ ligand (P1) and the hydride occupy the axial positions while the terminal phosphorus atoms P2 and P3 and triphenylphosphine (P4) are in equatorial position. The $^{31}P\{^1H\}$NMR spectrum at 243 K of **1c** consists of three multiplets. The resonance corresponding to P1 appear at 59.9 ppm and is split into a doublet by P4 (19 Hz). This doublet is in turn split into a triplet by the coupling to P2 and P3 (6 Hz). In the proton-coupled ^{31}P NMR spectrum an additional 169 Hz coupling between P1 and the hydride is observed. The size of the two bond P–H coupling indicates a linear P–Pt–H arrangement [11]. The size of the Pt–P1 coupling (1770 Hz) is in keeping with the *trans*-influence effect.

The signal at 7.3 ppm is assigned to P4 and is split into a doublet of doublets of doublets attributable to coupling to P1 (19 Hz) and to the inequivalent phosphorus atoms P2 and P3. The couplings P2–P4 and P3–P4 are 137 and 143 Hz compared with typical values of ca. 300 Hz and ca. 10 Hz for P–Pt–P angles of 180° (*trans*) and 90° (*cis*) respectively [12,13]. The terminal phosphorus atoms P2 and P3 are isochronous, at 7.05 T (33.6 ppm). The Pt–P coupling constants involving P2, P3 and P4 are relatively large as usually observed for the equatorial positions in a trigonal bipyramidal geometry [14].

The ^1H NMR signal of the hydride is a doublet of doublets of triplets due to the couplings to P1, P4 (20 Hz) and P2 and P3 (3 Hz). The chemical shift (−9.9 ppm) is surprisingly different from that reported for $[PtH\{P(CH_2CH_2PPh_2)_3\}]^+$ (−0.9 ppm) [15]. We therefore decided to reexamine this shift; we found the hydride resonance of $[PtH\{P(CH_2CH_2PPh_2)_3\}]^+$ to appear at −6.8 ppm (doublet of quartets, 162 and 12 Hz), which is closer to that for **1c**.

At ambient temperature, the ^{31}P NMR signal of PPh_3 is broadened and the Pt–P and P–P couplings involving triphenylphosphine disappear because of intermolecular PPh_3 exchange.

Synthesis of related compounds

Treatment of $[Pt\{PhP(CH_2CH_2PPh_2)_2\}(PBu_3)](O_3SCF_3)_2$ (**2a**) with $NaBH_4$ in ethanol–water or methanol–dichloromethane produces the hydride $[PtH\{PhP(CH_2CH_2PPh_2)_2\}(PBu_3)]^+$ (**2c**) exclusively. In aqueous tetrahydrofuran the hydride is formed as an intermediate but is converted into the zerovalent complex $[Pt\{PhP(CH_2CH_2PPH_2)_2\}(PBu_3)]$ (**2b**) within one hour. The NMR data for the compounds are listed in Table 1. In contrast to **1c**, $[PtH\{PhP(CH_2CH_2PPh_2)_2\}(PBu_3)]^+$ is stable towards dissociation on the ^{31}P NMR time scale at ambient temperature.

We also prepared the five-coordinate hydrido complexes $[PtH\{PhP(CH_2CH_2PPh_2)_2\}L]^+$, ($L = PPh_2H$, PCy_2H and $Ph_2PCH_2PPh_2$) by treatment of the corresponding complexes $[Pt\{PhP(CH_2CH_2PPh_2)_2\}L](O_3SCF_3)_2$ with $NaBH_4$ in methanol–dichloromethane.

References

1 T. Yoshida and S. Otsuka, J. Am. Chem. Soc., 99 (1977) 2134.
2 T. Yoshida, T. Matsuda, T. Okano, T. Kitani and S. Otsuka, J. Am. Chem. Soc., 101 (1979) 2027.
3 L. Manojlovic-Muir, I.R. Sobe, S.S.M. Ling, A.J. McLennan and R.J. Puddephatt, J. Chem. Soc., Chem. Commun., (1985) 1725.
4 R.A. Schunn, Inorg. Chem., 15 (1976) 208.
5 A.D. English, P. Meakin and J.P. Jesson, J. Am. Chem. Soc., 98 (1976) 422.
6 K.N. Harrison, P.A.T. Hoye, A.G. Orpen, P.G. Pringle and M.B. Smith, J. Chem. Soc., Chem. Commun., (1989) 1096.
7 A. Handler, P. Peringer and E.P Müller, J. Chem. Soc., Dalton Trans., (1990) 3725.
8 K.D. Tau and D.W. Meek, Inorg. Chem., 18 (1979) 3574.
9 J. Chatt, R. Mason and D.W. Meek, J. Am. Chem. Soc., 97 (1975) 3826; L.M. Green, Y. Park and D.W. Meek, Inorg. Chem., 27 (1988) 1658.
10 C.A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini and J.A. Ramirez, J. Chem. Soc., Chem. Commun., (1989) 304.
11 H.C. Clark and K.R. Dixon, J. Am. Chem. Soc., 91 (1969) 596.
12 P.S. Pregosin and R.W. Kunz, in P. Diehl, E. Fluck and R. Kosfeld (Eds.), ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes, Springer, Berlin, 1979.
13 K.R. Dixon, in S. Mason (Ed.), Multinuclear NMR, Plenum Press, New York, 1987.
14 P. Meakin and J.P. Jesson, J. Am. Chem. Soc., 96 (1974) 5751.
15 P. Brüggeller, Inorg. Chim. Acta, 129 (1987) L 27.